AD-740 861

GRADUATE SCHOOL OF OCEANOGRAPHY
UNIVERSITY OF RHODE ISLAND
KINGSTON, RHODE ISLAND

Reproduction of the material contained in this report in whole or in part is permitted for any purpose of the United States Government

Distribution of this document is unlimited

Fluoride Chlorinity Ratios in Narragansett Bay

Ref. No. 72-1

by

Gerard R. Miller, Jr., Kyle Woosley, and Dana R. Kester

Approved for distribution

Sponsored by Office of Naval Research

Report under Contract No. N00014-68-A-0215-0003

February 1972

Best Available Copy

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Graduate School of Oceanography University of Rhode Island Kingston, Rhode Island 02881	2a. REPORT SECURITY CLASSIFICATION 2b. GROUP

3. REPORT TITLE

Fluoride Chlorinity Ratios in Narragansett Bay

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Technical Report

5. AUTHOR(S) (First name, middle initial, last name)

Gerard R. Miller, Jr., Kyle Woosley, and Dana R. Kester

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
February 1972	16	17

8a. CONTRACT OR GRANT NO. ONR N00014-68-A-0215-0003 b. PROJECT NO. c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) 72-1 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT

Distribution of this document is unlimited

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY

13. ABSTRACT

Fluoridation of domestic water supplies contributes a significant portion of the total fluoride at the head of Narragansett Bay. Fluoride and chlorinity measurements were made at twelve stations in Narragansett Bay to evaluate their use as chemical tracers in this estuarine environment. The ratio of fluoride to chlorinity ranged from 6.7 to 8.3 x 10^{-5} mg F/Cl°/₀₀. The observations indicate that fluoride mixes conservatively along the main axis of the Bay and there was not sufficient evaporation or fluoride removal to be detected in the plot of fluoride-chlorinity ratio versus 1/Cl°/₀₀.

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0102-014-6600

Security Classification

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Fluoride						
Fluoride-chloride ratio						
Narragansett Bay Fluoride						
Estuarine Fluoridated Waters						

DD FORM 1 NOV 65 1473 (BACK)
(PAGE 2)

Security Classification

ABSTRACT

Fluoridation of domestic water supplies contributes a significant portion of the total fluoride at the head of Narragansett Bay. Fluoride and chlorinity measurements were made at twelve stations in Narragansett Bay to evaluate their use as chemical tracers in this estuarine environment. The ratio of fluoride to chlorinity ranged from 6.7 to 8.3 x 10^{-5} mg F/Cl°/₀₀. The observations indicate that fluoride mixes conservatively along the main axis of the Bay and there was not sufficient evaporation or fluoride removal to be detected in the plot of fluoride-chlorinity ratio versus 1/Cl°/₀₀.

INTRODUCTION

The fluoridation of domestic water supplies at the head of Narragansett Bay represents a significant input of fluoride to the Bay. The Blackstone, Providence, and Pawtuxet Rivers are the main sources of fresh water in this region (U. S. Geological Survey, 1969; Hess, 1970) and these rivers contain 0.2 mg F/l (U. S. Geological Survey, 1958). The natural input of fluoride by these sources is 3.1 g F/sec during July (the period to be considered in this report) and is 8.1 g F/sec annually. The addition of fluoridated water (1 mg F/l) through the domestic water supplies and sewage treatment plants of Cumberland, East Providence, Pawtucket, Providence, and Woonsocket contributes 2.9 g F/sec throughout the year. Thus, fluoridation doubles the natural input of fluoride at the head of Narragansett Bay during July and amounts to 36% of the natural input annually.

Even though the quantities of fluoride added to estuarine waters by fluoridation can be comparable to the natural input, this addition of fluoride probably does not constitute a pollution threat. Seawater contains 1.3 mg F/l, whereas fluoridated domestic water contains 1 mg F/l. Marine organisms should thus be able to tolerate the fluoride concentrations of fluoridated waters, and this level of fluoride is not known to be toxic (Eagers, 1969; Moore, 1971).

The enrichment of fluoride in estuaries by fluoridation, and the generally greater proportion of fluoride to other dissolved substances in fresh waters than in seawater, suggests that fluoride may be a useful chemical tracer of processes in the estuarine environment. In the open ocean the ratio of fluoride to chlorinity, $F/Cl^{\circ}/_{oo}$, is constant with only unusual exceptions (Greenhalgh and

Riley, 1963; Riley, 1965; Brewer, Spencer, and Wilkniss, 1970; Bewers, 1971; Kester, 1971a). Chlorinity is a measure of the chloride (and bromide) in the water, and it is directly related to the salinity, $S^{\circ}/_{oo}$, by $S^{\circ}/_{oo} = 1.80655\ Cl^{\circ}/_{oo}$ (Riley and Chester, 1971). In estuaries, the $F/Cl^{\circ}/_{oo}$ ratio should vary with the extent of mixing between the seawater and fresh water. A correlation between $F/Cl^{\circ}/_{oo}$ and $1/Cl^{\circ}/_{oo}$ will reveal conservative mixing (Fig. 1). The depletion of fluoride (e.g., precipitation) without the loss of water would transpose the points of the conservative mixing curve to lower values along the ordinate (curve C of Fig. 1). The loss of water (e.g., evaporation) without the removal of fluoride would move the points of curve B to lower values along the abscissa (curve A of Fig. 1). In this work we have examined the occurrence of fluoride in Narragansett Bay to test its usefulness as a chemical tracer during the mixing of seawater and fresh water. Windom (1971) reported a study of fluoride in coastal waters of Georgia in which the influence of river runoff was detectable up to chlorinities of $10\text{-}11^{\circ}/_{oo}$. The concentration of fluoride in Georgia rivers was reported as 0.05 to 0.08 ppm (mg/kg). He found evidence of the removal of fluoride from the estuary by sediments.

METHODS

Sea water samples were collected from several depths (0, 3, 6, 12, 20 m) on 9 July 1971 at twelve stations in Narragansett Bay (Fig. 2). The samples were obtained with 5-liter Niskin bottles at the surface and within one meter of the bottom and with 1.3-liter Nansen bottles at intermediate depths.

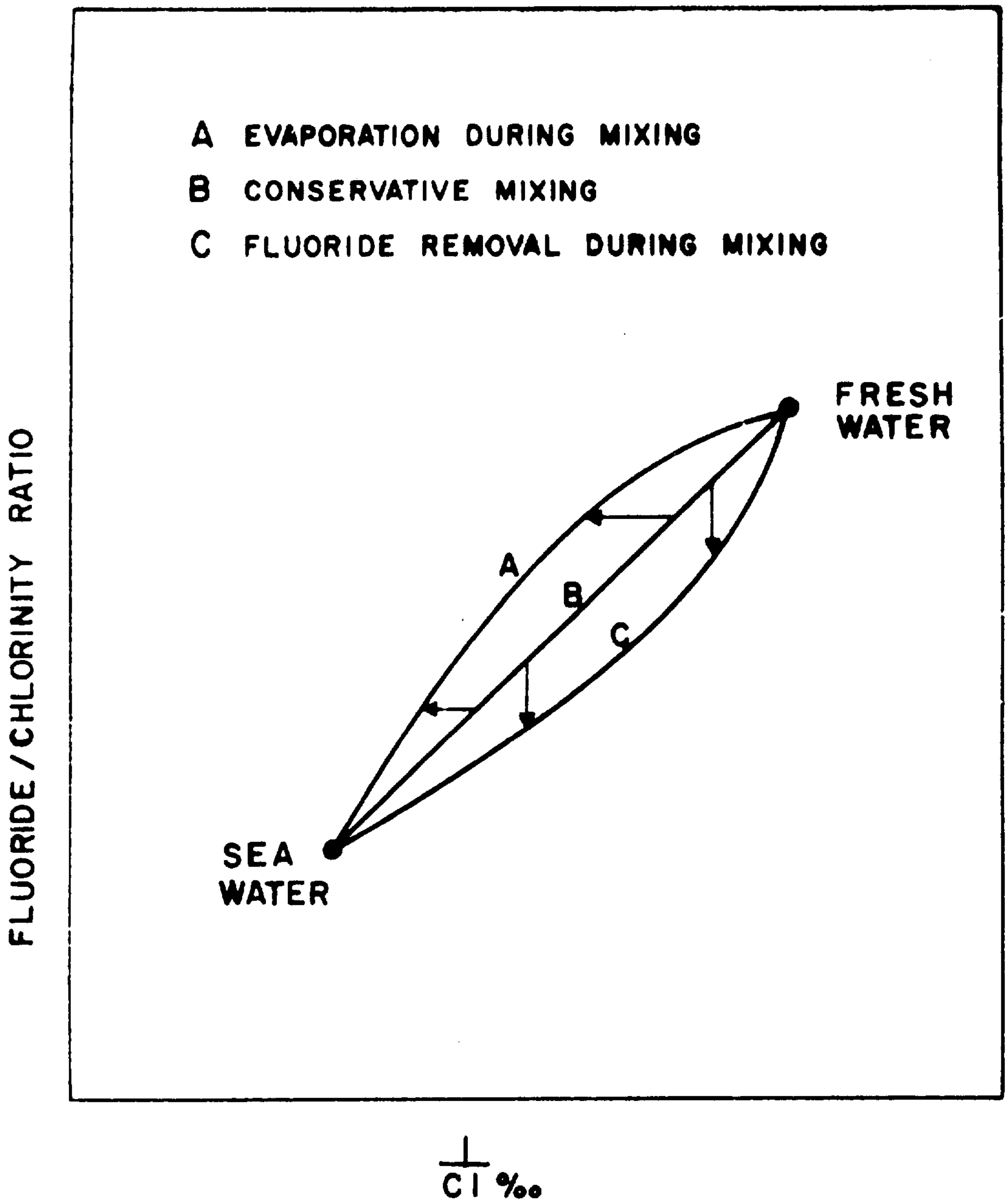
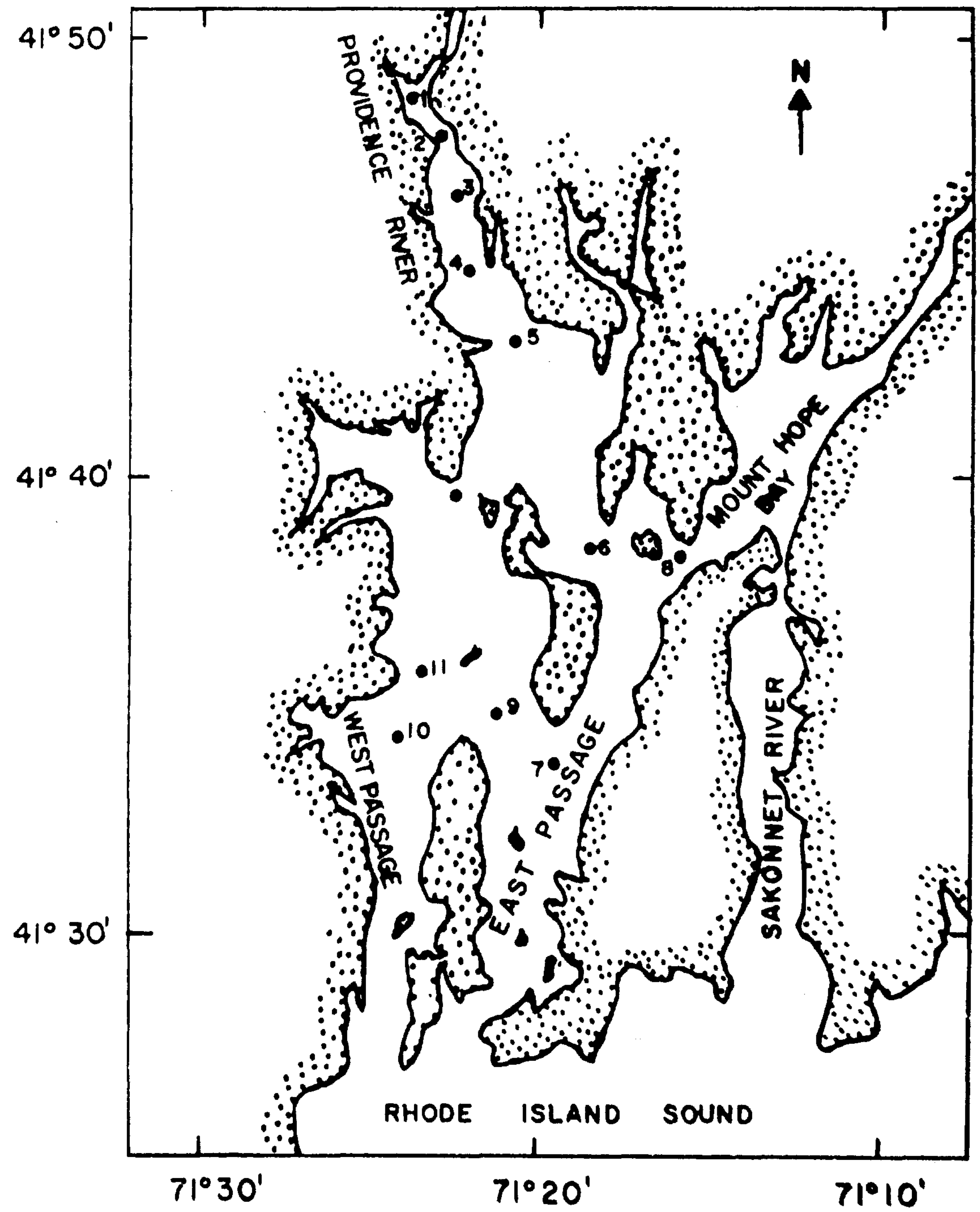


Figure 1. Mixing curves for fresh and seawater showing evaporation of water without loss of fluoride (A), conservative wiping (B), and removal of fluoride without loss of water (C).

Figure 2. Station locations in the Providence River and Narragansett Bay, Rhode Island.



Fluoride samples were stored in 125 ml polyethylene bottles which had been washed with 2 N HCl and soaked with filtered seawater. Salinity samples were placed in 250 ml glass screw cap bottles. The samples were not filtered in order to detect both suspended and dissolved fluoride. All analyses were performed within one week of collection.

The fluoride measurements were made using the lanthanum-alizarin complexone method of Greenhalgh and Riley (1961). Standard fluoride solutions (1.1, 1.3, and 1.5 mg F/l as NaF) were measured with each set of samples to account for any variation in the reagents or the Beckman DU-2 spectrophotometer. The fluoride concentration was expressed as mg of fluoride per kg of seawater so that the values and the fluoride-chlorinity ratios were independent of temperature. The precision of the analysis was 1.5%, based on two standard deviations of day-to-day replicate determinations (Kester, 1971b).

Chlorinity and salinity were based on measurements of the conductivity ratio to Copenhagen Standard Sea Water using an inductive salinometer and the International Oceanographic Tables (UNESCO, 1966).

RESULTS AND DISCUSSION

Some of the physical aspects of Narragansett Bay have been summarized by Hicks (1959) and Hess (1970). The primary source of fresh water to Narragansett Bay during the summer is in the vicinity of the Providence River. The salinity at station 12 was remarkably uniform with depth (29.30°/₀₀ at the surface, 29.74°/₀₀ within one meter of the bottom), while a larger gradient occurred at station 6 (28.83°/₀₀ at the surface, 30.63°/₀₀

near the bottom). This observation along with the salinity data at the other stations indicates that during our period of observation the stratified low salinity water flowed from the Providence River to the East Passage. Any flow of low salinity water past station 12 was accompanied by vertical mixing, probably by tidal action, within the narrow constriction. Haight (1938) reported currents of up to one knot at this location. Similar observations at station 8 (29.40°/$_{oo}$ at the surface, 30.20°/$_{oo}$ at the bottom) indicate any low salinity flow from Mount Hope Bay is associated with strong vertical mixing before it reaches the East Passage. Thus, in the examination of fluoride as a chemical tracer in the Bay, it is most useful to consider stations 1-7.

The distribution of salinity from stations 1 to 7 is shown in Fig. 3. Typical estuarine flow is evident with water from Rhode Island Sound wedged beneath the lower salinity water of the Providence River. The low salinity contribution, and hence the greatest mixing effects, occur primarily in the upper six meters at these stations. The fluoride-chlorinity ratio is shown versus 1/Cl°/$_{oo}$ for these waters in Fig. 4. The less saline waters are clearly enriched with fluoride relative to chloride, which may result from either the input of fluoridated domestic waters or fluoride rich natural waters. Most of the data fall within the 95% confidence limits of a least squares linear regression, and there appears to be no significant curvature which would result from evaporation or fluoride removal. Points A and B show the greatest departure from the overall trend. These data are from 0 and 3 m at station 5. A plot of fluoride concentration versus salinity (Fig. 5) reveals that these samples contain approximately 4% more fluoride than the other samples, and hence they are anomalous due to their fluoride content and

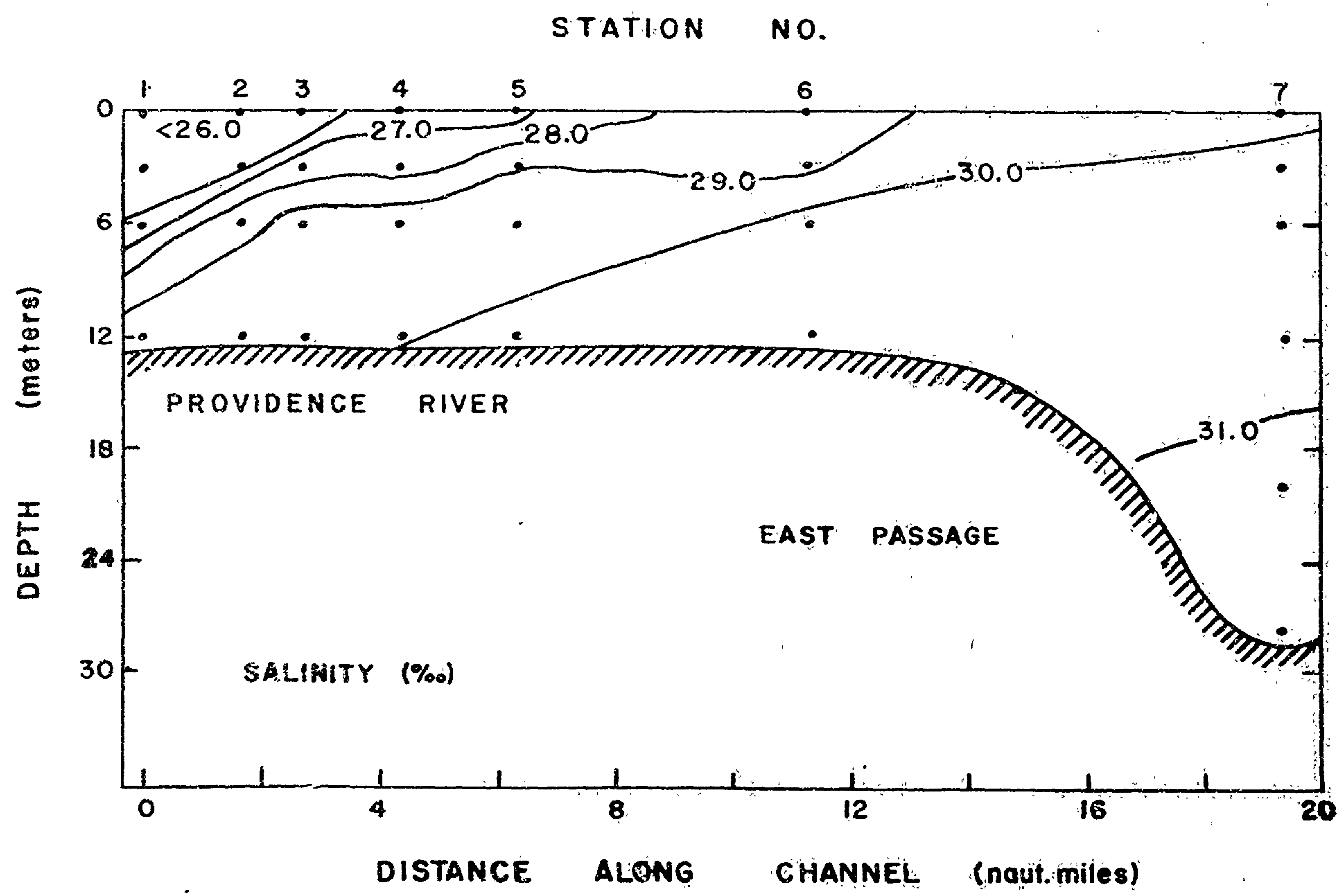


Figure 3. Salinity distribution in the Providence River and East Passage of Narragansett Bay, 9 July 1971.

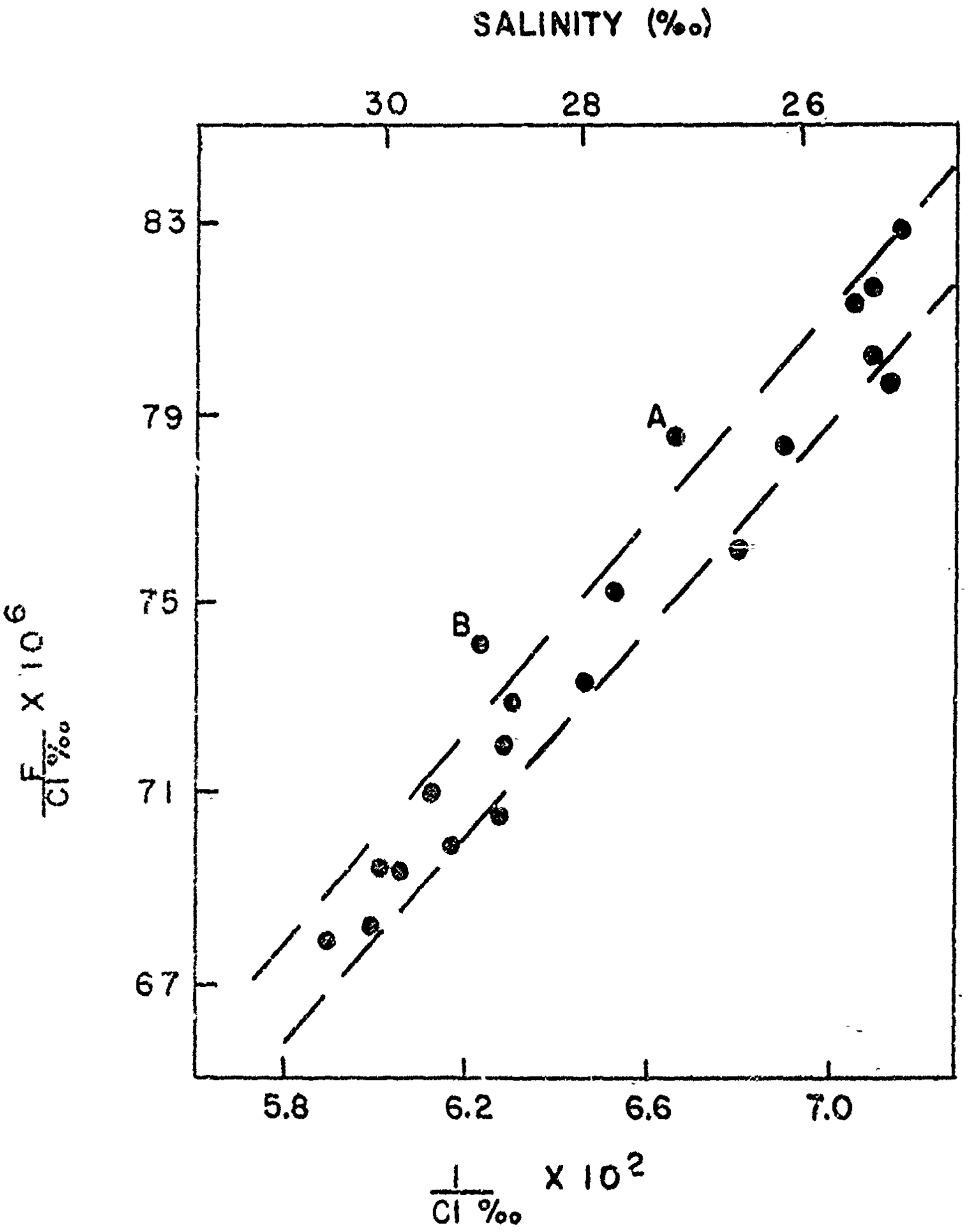
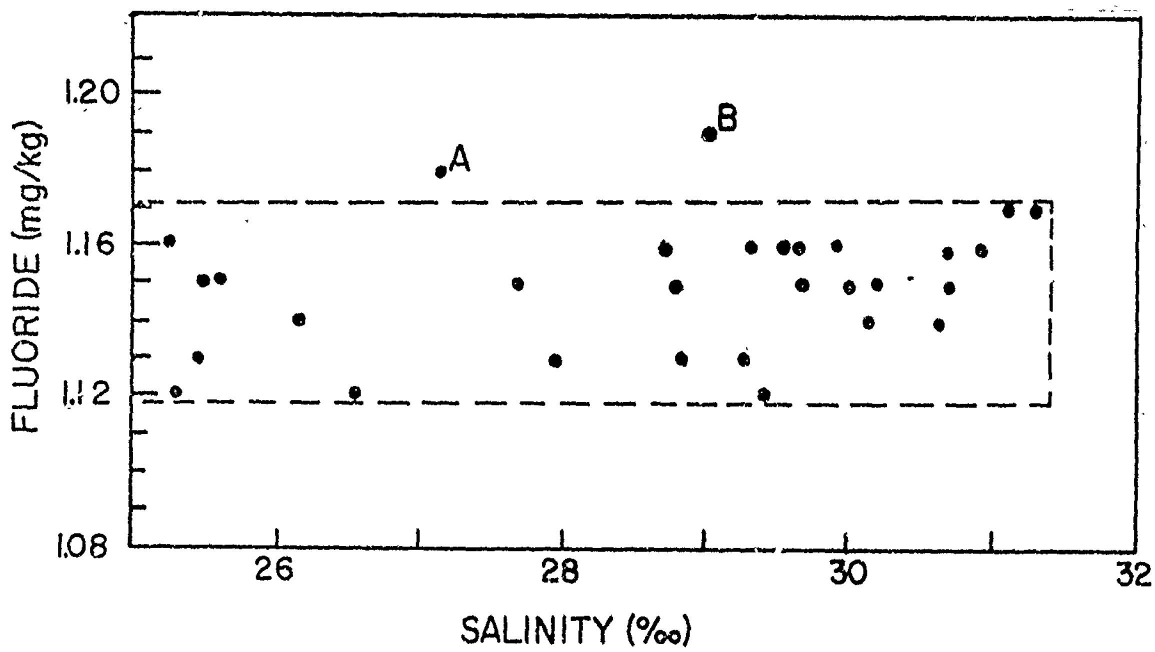


Figure 4. Fluoride chlorinity ratio versus inverse chlorinity in Narragansett Bay. Points A and B are from 0 and 3 m at station 5, 9 July 1971.

Figure 5. Plot of fluoride concentration versus salinity in Narragansett Bay. Points A and B are from 0 and 3 m at station 5, 9 July 1971.



not due to their chlorinity. We have not been able to identify a source of this excess fluoride.

One remarkable feature about the fluoride distribution is that even though the fresh water input reduces the salinity of the incoming seawater by 20%, the fluoride concentration varies by less than 2% (except for 0 and 3 m at station 5). The fluoride content of the fresh water, therefore, is comparable to that of the seawater (approximately 1 mg/l) which is typical of fluoridated, rather than natural, fresh water. The observations of the fluoride-chlorinity ratio in Narragansett Bay indicate that fluoride mixes conservatively along the main axis of the Bay and there was not sufficient evaporation or fluoride removal during the early part of July 1971 to be detected in the plot of fluoride-chlorinity ratio versus $1/Cl^{o}/_{oo}$.

REFERENCES

Bewers, J.M. 1971. North Atlantic fluoride profiles. Deep-Sea Res. 18: 237-241.

Brewer, P.G., D.W. Spencer, and P.E. Wilkniss. 1970. Anomalous fluoride in the North Atlantic. Deep-Sea Res. 17: 1-7.

Eagers, R.Y. 1969. Toxic properties of inorganic fluorine compounds. Elseiver Publ., London, 158 pp.

Greenhalgh, R. and J.P. Riley. 1961. The determination of fluorides in natural waters with particular reference to sea water. Analytica Chim. Acta 25: 179-188.

Greenhalgh, R. and J.P. Riley. 1963. Occurrence of abnormally high fluoride concentrations at depth in the ocean. Nature, Lond. 197: 371-372.

Haight, F.J. 1938. Currents in Narragansett Bay, Buzzards Bay, and Nantucket and Vineyard Sounds. Coast and Geodetic Survey. Special Publication No. 208, 103 pp.

Hess, K.W. 1970. Narragansett Bay: An example in estuary classification. Sea Grant Publication No. 4, Department of Ocean Engineering, Univ. of Rhode Island, 39 pp.

Hicks, S.D. 1959. The physical oceanography of Narragansett Bay. Limnol. Oceanogr. 4 (3): 316-327.

Kester, D.R. 1971a. Fluoride chlorinity ratio of sea water between the Grand Banks and the Mid-Atlantic Ridge. Deep-Sea Res. 18: 1123-1126.

Kester, D.R. 1971b. Fluoride analyses in the Northwest Atlantic Ocean. Univ. of Rhode Island, Graduate School of Oceanography, Technical Report No. 71-2, 14 pp.

Moore, D.J. 1971. The uptake and concentration of fluoride by the blue crab, Callinectes sapidus. Chesapeake Science 12: 1-13.

Riley, J.P. 1965. The occurrence of anomalously high fluoride concentrations in the North Atlantic. Deep-Sea Res. 12: 219-220.

Riley, J.P. and R. Chester. 1971. Introduction to marine chemistry. Academic Press, London, 465 pp.

UNESCO. 1966. International Oceanographic Tables. UNESCO Office of Oceanography.

U.S. Geological Survey. 1969. Surface water records for Massachusetts, New Hampshire, Rhode Island, and Vermont. U.S. Dept. of the Interior, Washington, D. C.

U.S. Geological Survey. 1958. Water Supply Paper No. 1571. U.S. Dept. of the Interior, Washington, D. C.

Windom, H.L. 1971. Fluoride concentration in coastal and estuarine waters of Georgia. Limnol. Oceanogr. 16 (5): 806-810.

ACKNOWLEDGEMENTS

We would like to acknowledge the assistance of Janice M. Stearns and Brendan T. Doherty in the collection of samples and of NEMRIP (U.R.I. Sea Grant Program) in providing background data. Participation of K. Woosley was possible through the National Science Foundation High School Student Summer Program in Marine Science at U.R.I. Portions of our work were supported by the Office of Naval Research under contract No. N00014-68-A-0215-003.

TABLE 1

Fluoride and Fluoride Chlorinity Ratios in Narragansett Bay

Station	Depth m	F mg/kg	Salinity °/oo	F/Cl x 10^5 g/kg - Cl°/oo
1	0	1.12	25.32	7.95
	3	1.13	25.46	8.02
	6	1.14	26.17	7.83
	12	1.12	29.44	6.85
2	0	1.16	25.24	8.28
	3	1.15	25.59	8.13
	6	1.15	28.76	7.20
	12	1.16	29.60	7.07
3	0	1.15	25.48	8.16
	3	1.15	27.68	7.52
	6	1.13	29.26	6.99
	12	1.15	29.65	6.99
4	0	1.12	26.55	7.61
	3	1.13	27.95	7.33
	6	1.16	28.70	7.29
	12	1.15	29.98	6.94
5	0	1.18	27.13	7.85
	3	1.19	28.99	7.41
	6	1.16	29.53	7.10
	12	1.15	30.18	6.86
6	0	1.13	28.83	7.06
	3	1.13	28.82	7.07
	6	1.14	30.13	6.81
	12	1.14	30.63	6.75
7	0	1.15	29.90	6.94
	3	1.15	30.06	6.94
	6	1.15	30.70	6.79
	12	1.16	30.88	6.78
	20	1.17	31.09	6.79
	28	1.17	31.28	6.75
8	0	1.12	29.40	6.89
	3	1.13	29.42	6.92
	6	1.12	29.53	6.88
	12	1.12	29.98	6.76
	23	1.12	30.20	6.71

TABLE 1 (Continued)

Station	Depth m	F mg/kg	Salinity °/oo	F/Cl x 10^5 g/kg - Cl°/oo
9	0	1.15	29.98	6.94
	3	1.15	29.98	6.96
	7	1.16	30.67	6.86
10	0	1.15	29.96	6.95
	3	1.15	29.95	6.93
	6	1.16	30.47	6.87
11	0	1.16	29.74	7.03
	3	1.15	29.79	7.00
	6	1.16	30.06	6.97
	7	1.15	30.53	6.83
12	0	1.16	29.30	7.12
	3	1.16	29.36	7.12
	6	1.15	29.58	7.03
	12	1.16	29.74	7.06
	21	1.16	29.88	7.03